

# Proton Affinities of Polybenzenoid Aromatic Hydrocarbons and Those with Five-Membered Rings

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## ABSTRACT

Proton affinities of PAHs including one five-membered ring are calculated by using the AM1 Hamiltonian for the determination of  $\Delta H_f^\circ$  of the neutral and protonated molecules. The calculated PAs are compared to experimental PAs measured by chemical ionization mass spectrometry, using a new method based on competition between charge transfer and proton transfer occurring during the ionization process. A procedure is proposed to validate AM1-calculated PAs from experimental PAs after rescaling the calculated and measured PA values. The site of protonation is first determined on the criterion of the lowest loss of aromaticity, then on the criterion of the largest HOMO coefficient. For indene, the corrected result is compared to an *ab initio* calculation at the MP2/6-31G\*//HF/6-31G\* level and to a DFT calculation at the B3LYP/6-31G\* and the B3LYP/6-311 + G\*\* levels. Five new PAs are thus established and one published experimental PA is revised. © 1997 by John Wiley & Sons, Inc.

## Introduction

P olycyclic aromatic hydrocarbons (PAHs) are ubiquitous environmental pollutants known to be toxic and mutagenous<sup>1,2</sup> at the ppt level. This explains why their emission is regulated and their occurrence is monitored. However, the determination of PAHs in the environment is made difficult by the existence of isomers that are hard

to distinguish analytically either by chromatography or by mass spectrometry.<sup>3–5</sup>

Chemical ionization (CI) with ammonia allows to differentiate the mass spectra of PAH isomers from the molecular and protonated molecular ion abundances.<sup>6</sup> The ionization mechanisms leading to the formation of these ions rely on the relative proton affinities (PAs).

Many PAs are not known.<sup>7</sup> They are difficult to measure experimentally by classical methods. In a previous study,<sup>6</sup> we have proposed a new procedure for experimental PAH proton affinities determination based on the direct measurement of the

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$M^{++}$  and  $[M + H]^+$  ion abundances in CI mass spectra. Our experimental results,<sup>6</sup> together with published data,<sup>7</sup> were observed to be consistent with the semiempirical proton affinity calculations carried out with AM1<sup>8</sup> and PM3<sup>9</sup> Hamiltonians for PAHs bearing only six-membered rings. However, a systematic discrepancy was observed for PAHs whose structure includes a five-membered ring. This discrepancy is only due to the semiempirical calculation of the enthalpy of formation of the neutral species.

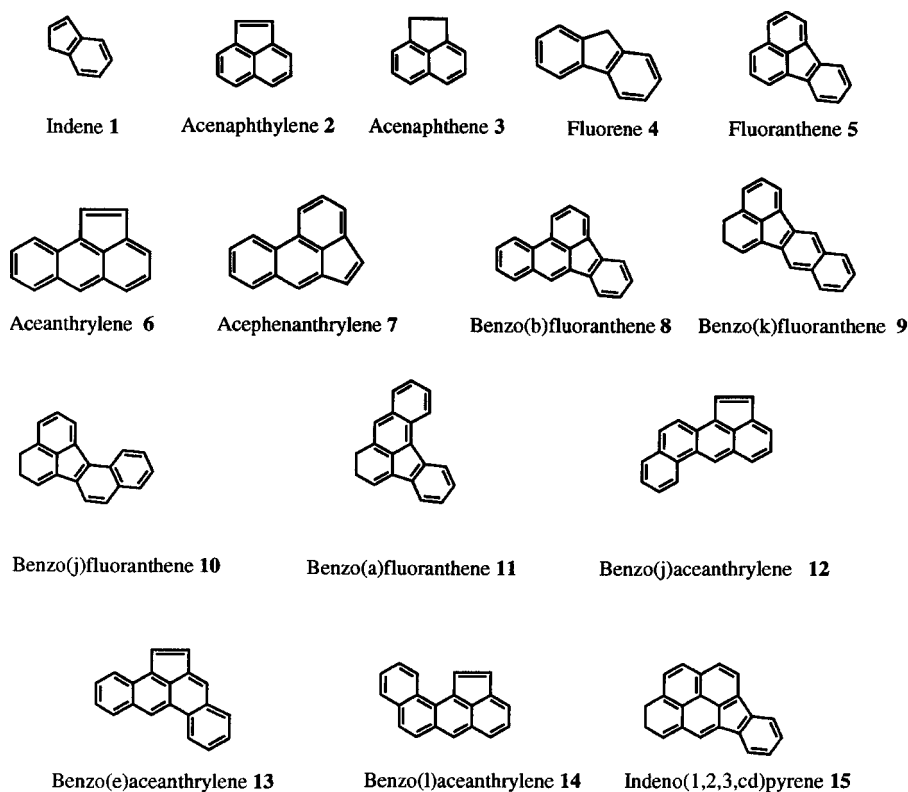
In this present article, semiempirical proton affinity calculations were performed systematically on PAHs with five-membered rings, some of which are considered as priority pollutants by the U.S. EPA. Scheme 1 illustrates the structures of the different molecules studied in this work. For the calibration of our semiempirical determination, high level *ab initio* calculation and DFT calculations were also performed, limited to the smallest molecule, indene **1**. As PAHs *ab initio* calculations are time consuming, only few low level calculations have been reported.<sup>10,11</sup> Finally, calculated PAs were compared with experimental values in

the literature,<sup>7</sup> and newly determined after our method.<sup>6</sup>

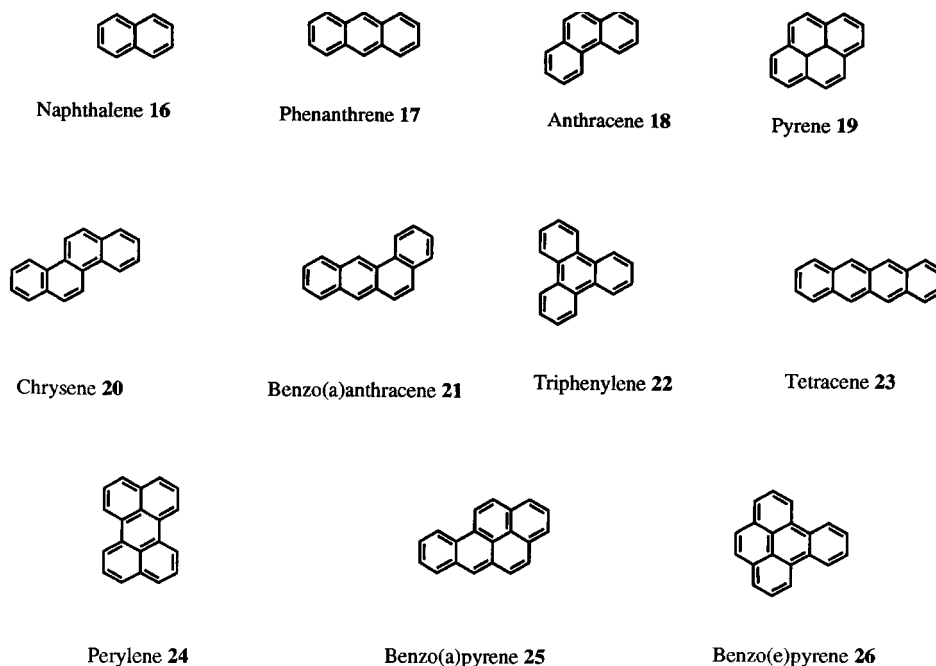
## Experimental Determination of Proton Affinities

Ammonia chemical ionization mass spectra of all PAHs have been performed on a HP5890 gas chromatograph (Hewlett Packard, Avondale, PA) connected to a HP5972 mass spectrometer operated in the CI mode, with  $NH_3$  as a reactant gas. A 30-m-long, 0.25-mm-i.d., 0.25- $\mu$ m film thickness DB5 column (J & W, Arcueil, France) was used with He as a carrier gas at an outlet flow rate of 1 mL/min. The mass spectrometer source temperature and pressure were set at 200°C and 213 Pa (1.6 Torr). For the sake of consistency, both experimental and calculated PAs will be defined relatively to the 204 kcal/mol value for ammonia recommended by Lias et al.<sup>7</sup>

Charge exchange with PAHs may occur if protonation is not possible. The ionization pathway will be different according to the PA of the PAH



SCHEME 1.



## SCHEME 2.

relative to ammonia. The relative intensities of the molecular peak,  $M^{+}$ , and the protonated molecular peak,  $[M + H]^+$ , observed under ammonia chemical ionization have been compared with the available experimental PAs (Table I, Fig. 1a, Scheme 2). Three situations are possible:

1. When the PAH proton affinity is above that of ammonia, protonation occurs and charge exchange is limited because of the large predominance of  $NH_4^+$  over  $NH_3^{+}$  within the source.
2. When the PAH proton affinity is lower than that of ammonia, protonation cannot occur and charge exchange predominates. The  $[M + 1]^+$  peak is observed at the exact abundance of the isotopic  $^{13}C$  contribution.
3. For PAHs with PAs close to ammonia, both protonation and charge exchange occur. A small variation of PA yields to a significant variation of the  $[M + 1]^+/M^{+}$  ratio<sup>6</sup> as shown in Figure 1a and enlarged Figure 1b.

This part of the curve can be examined as a straight line with a regression coefficient of  $R = 0.99$ . Unknown PAs can then be estimated with good accuracy from the  $[M + 1]^+/M^{+}$  ratio through the linear equation:

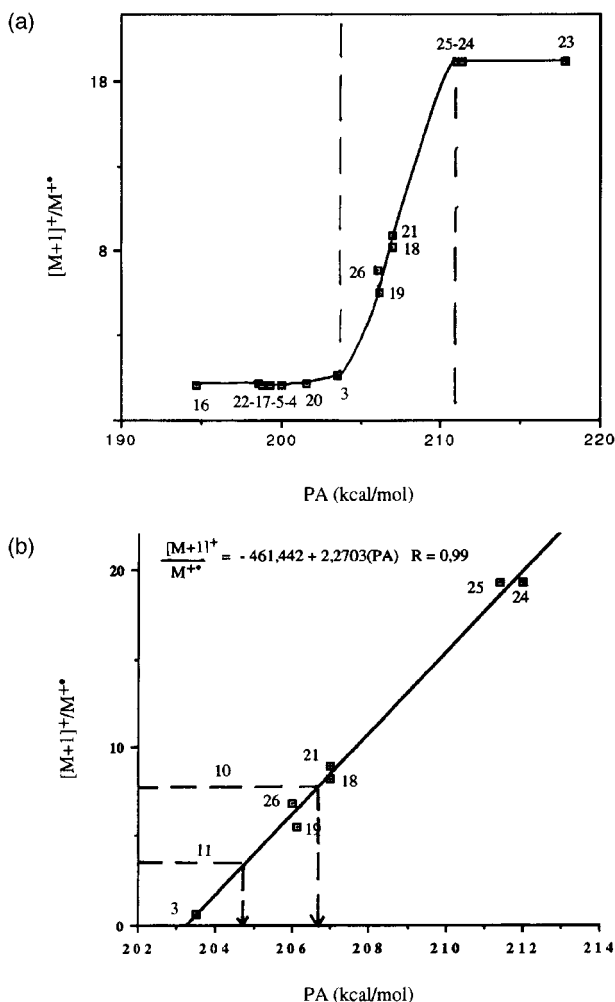
$$[M + 1]^+/M^{+} = -461.44 + 2.27 \text{ PA}$$

**TABLE I.**  
Experimental PAs of Five and Six-Membered-Ring PAHs (kcal / mol).

Compound	PA
Indene 1	—
Acenaphthylene 2	—
Acenaphthene 3	203.5 <sup>a</sup>
Fluorene 4	200.0 <sup>a</sup>
Fluoranthene 5	199.3 <sup>a</sup>
Aceanthrylene 6	—
Acephenanthrylene 7	—
Benzo(b)fluoranthene 8	—
Benzo(k)fluoranthene 9	—
Benzo(a)fluoranthene 10	—
Benzo(j)fluoranthene 11	—
Benzo(j)aceanthrylene 12	—
Benzo(e)aceanthrylene 13	—
Benzo(l)aceanthrylene 14	—
Indeno(1,2,3cd)pyrene 15	—
Naphthalene 16	194.7 <sup>a</sup>
Phenanthrene 17	198.7 <sup>a</sup>
Anthracene 18	207.0 <sup>a</sup>
Pyrene 19	206.1 <sup>a</sup>
Chrysene 20	201.6 <sup>a</sup>
Benzo(a)anthracene 21	207 <sup>b</sup>
Triphenylene 22	198.5 <sup>a</sup>
Tetracene 23	217.8 <sup>a</sup>
Perylene 24	211.4 <sup>a</sup>
Benzo(a)pyrene 25	212 <sup>b</sup>
Benzo(e)pyrene 26	206 <sup>b</sup>

<sup>a</sup> From ref. 7.

<sup>b</sup> From ref. 6.

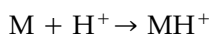


**FIGURE 1.** (a) Plot of the experimental  $[M + 1]^+ / M^+$  peak ratio versus the proton affinity for PAHs including five-membered rings. Identification numbers as in Scheme 1. (b) Enlarged portion of curve (a). Dotted lines exemplify new PA determinations for Benzo(a)fluoranthene **10** and benzo(j)fluoranthene **11**.

This method constitutes the best available experimental mean to determine the proton affinities of large PAHs, although it requires that the PA of the reactant gas be close to that of the PAH.

## Computations

PA is defined as the negative of the enthalpy change of the reaction:



thus:

$$PA = \Delta H_f^\circ(M) + \Delta H_f^\circ(H^+) - \Delta H_f^\circ(MH^+)$$

The computation of PA requires energies of formation of the neutral and protonated molecules. The experimental value of the heat of formation of  $H^+$  was set at 367.2 kcal/mol<sup>12</sup> in all our semiempirical calculations because  $\Delta H_f^\circ(H^+)$  is poorly evaluated by AM1.

Calculations were performed using AM1 as implemented in the MOPAC version 6.0 program for aromatic hydrocarbons described on Scheme 1. This gives the standard enthalpies of formation at 298 K,  $\Delta H_f^\circ$ , expressed in kilocalories per mole.

A comparison between semiempirical AM1 and *ab initio* results was conducted for the smallest molecule studied, indene **1**. Several different protonation sites were tested with the *ab initio* method for confirming the AM1 results.

*Ab initio* calculation computations employed the GAUSSIAN 94 computer program.<sup>13</sup> The structures of indene and protonated indene were fully optimized at the HF/6-31G\* level using the AM1 geometry as the initial structure. AM1 and *ab initio* geometries were found not to differ significantly. Optimized structures were then used for single-point energy calculations at the MP2/6-31G\* level. Vibrational frequencies, calculated at the HF/6-31G\* level, verified the nature of the stationary points as minima and allowed to obtain the zero point energies (ZPEs).

The complexation energy ( $E_{\text{compl}}$ ) was calculated after the relationship:

$$M + H^+ \rightarrow MH^+ \\ E_{\text{compl}} = E_{\text{ab initio}}(MH^+) - E_{\text{ab initio}}(M)$$

For the sake of comparison of *ab initio* calculations with experimental results or AM1 determinations, energies must be corrected thermodynamically to standard temperatures. Thermal energy ( $E_{\text{therm}}$ ) corrections of translational, rotational, and vibrational contributions to the internal energy of both the neutral and protonated species have been determined from frequency calculations<sup>14</sup>:

$$\Delta E_{\text{therm}} = E_{\text{therm}}(MH^+) - E_{\text{therm}}(M) - E_{\text{therm}}(H^+) \\ E_{\text{therm}}(H^+) = -\frac{3}{2}RT$$

The internal energy change at standard temperature is:

$$\Delta U(T) = E_{\text{compl}} + \Delta E_{\text{therm}} \text{ at } 298 \text{ K}$$

The enthalpy change corresponding to the negative of the proton affinity is obtained from the relationship:

$$\Delta H(T) = -PA_M = \Delta U(T) + RT\Delta n$$

DFT calculations were then carried out for indene **1** and protonated indene at the B3LYP/6-31G\* level. All corrections have been performed to obtain the PA value (at 298 K). A B3LYP/6-311+G\*\* calculation was also performed, but the thermal corrections from B3LYP/6-31G\* were applied. Scale factors were never used.

## Results and Discussion

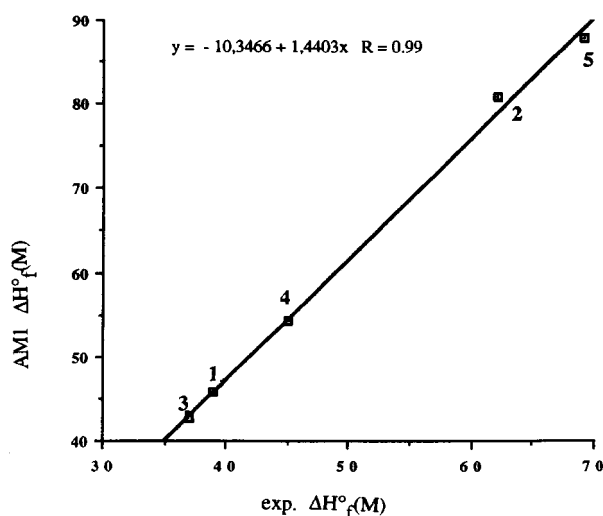
### NEUTRAL PAHS

Table II compares  $\Delta H_f^\circ(M)$  computed with the AM1 Hamiltonian and experimental data with available data.<sup>7</sup> AM1 for  $\Delta H_f^\circ(M)$  values correlate to the experimental data with a regression coefficient of  $R = 0.99$  (Fig. 2). Analogous results were obtained previously with a series of PAHs including only six-membered rings. Again experimental and AM1-calculated  $\Delta H_f^\circ(M)$  values were correlated<sup>6</sup> linearly. Both correlations for the two series of homologous PAHs bearing only six-membered rings or having one five-membered ring follow different linear equations. Hence, both series should be considered separately. The contribution of the slight anaromaticity introduced by the five-membered ring could be responsible.

**TABLE II.** Experimental and AM1-Calculated  $\Delta H_f^\circ(M)$  (kcal/mol) for Five-Membered-Ring PAHs.

Compound	AM1	Exp.
Indene <b>1</b>	45.8	39 <sup>a</sup>
Acenaphthylene <b>2</b>	80.8	62 <sup>a</sup>
Acenaphthene <b>3</b>	42.6	37 <sup>a</sup>
Fluorene <b>4</b>	54.4	45 <sup>a</sup>
Fluoranthene <b>5</b>	87.9	69.2 <sup>a</sup>
Aceanthrylene <b>6</b>	103.2	—
Acephenanthrylene <b>7</b>	95.9	—
Benzo( <i>b</i> )fluoranthene <b>8</b>	103.2	—
Benzo( <i>k</i> )fluoranthene <b>9</b>	105.1	—
Benzo( <i>a</i> )fluoranthene <b>10</b>	111.4	—
Benzo( <i>j</i> )fluoranthene <b>11</b>	109.1	—
Benzo( <i>j</i> )aceanthrylene <b>12</b>	119.1	—
Benzo( <i>e</i> )aceanthrylene <b>13</b>	117.1	—
Benzo( <i>l</i> )aceanthrylene <b>14</b>	121.2	—
Indeno(123 <i>cd</i> )pyrene <b>15</b>	116.3	—

<sup>a</sup> From ref. 7.



**FIGURE 2.** Calculated versus experimental  $\Delta H_f^\circ(M)$  (kcal/mol) of molecules listed in Scheme 1.

### PROTONATED PAHS

The calculation of the  $\Delta H_f^\circ$  of the protonated PAHs requires that the protonation site be clearly defined because little information is available on that topic. For that purpose, we have calculated the  $\Delta H_f^\circ$  systematically for protonated PAH structures with the proton on each hydrogen-bearing carbon atom. Ring junction carbons have not been considered since their protonation would result in the loss of planarity and steric strain. The most stable protonated structure, corresponding to the lowest  $\Delta H_f^\circ$ , was selected for the PA calculation. An interpretation of the most energy-favored protonation site is discussed.

Carbon atoms of the neutral molecules studied can be classified into four different types:

- Carbons in a five-membered ring.
- Carbons bonded to two ring junction carbons.
- Carbons bonded to only one ring junction carbon.
- Carbons located between two hydrogen-bearing carbons.

### HOMO COEFFICIENTS

HOMO coefficients have been examined for each molecule. The largest coefficient is most often associated with carbons bonded to two ring junction carbon atoms (type b) when present, i.e., for acean-

thrylene 6, acephenanthrylene 7, benzo(*b*)fluoranthene 8, benzo(*k*)fluoranthene 9, and benzo(*a*)fluoranthene 11, benzo(*j*)aceanthrylene 12, benzo(*e*)aceanthrylene 13, and benzo(*l*)aceanthrylene 14. Only one exception is observed; the type (b) carbon of indeno(123*cd*)pyrene 15 does not have the largest HOMO coefficient, in this case it is located on a type (c) carbon.

If no type (b) carbon is present, generalization cannot be made. For indene 1 and acenaphthylene 2, the largest HOMO coefficient is located on type (a) carbon; for acenaphthene 3, fluoranthene 5, and benzo(*j*)fluoranthene 10, the HOMO coefficient is located on a type (c) carbon; and, for fluorene 4, the largest HOMO coefficient is located on a type (d) carbon.

BEST PROTONATION SITE

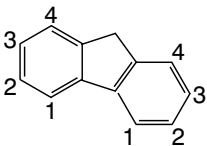
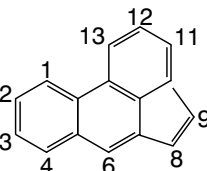
Rule 1

The lowest  $\Delta H_f^\circ(\text{MH}^+)$  value is obtained when the proton is located on a carbon of the five-membered ring [type (a)], because it perturbs the aromaticity of the molecule less. This is the case for indene 1, acenaphthylene 2, aceanthrylene 6, acephenanthrylene 7, benzo(*j*)aceanthrylene 12, benzo(*e*)aceanthrylene 13, and benzo(*l*)aceanthrylene 14.

Rule 2

If no type (a) carbon is available, the best protonation site corresponds to the carbon which bears

TABLE III.  
 $\Delta H_f^\circ(\text{MH}^+)$  (kcal / mol) and HOMO Coefficients for Each Carbon of Fluorene 4 and Acephenanthrylene 7.

<div></div> <div>Fluorene 4</div>			
C-position	Carbon type	HOMO coeff.	$\Delta H_f^\circ(\text{MH}^+)$
Fluorene			
1	c	0.27	227.1
2	d	0.19	230.9
3	d	0.39	224.1
4	c	0.11	233.3
<div></div> <div>Acephenanthrylene 7</div>			
Acephenanthrylene			
1	c	0.32	267.2
2	d	0.14	268.8
3	d	0.25	270.3
4	c	0.34	267.6
6	b	0.40	266.7
8	a	0.24	252.8
9	a	0.33	253.0
11	c	0.29	266.0
12	d	0.19	267.0
13	c	0.21	264.0

the largest HOMO coefficient. This is the case for acenaphthene **3**, fluorene **4**, fluoranthene **5**, benzo(*j*)fluoranthene **10**, benzo(*a*)fluoranthene **11**, and indeno(123*cd*)pyrene **15** (Table IV).

For indene **1** and acenaphthylene **2**, both rules are followed.

### Exceptions

For benzo(*b*)fluoranthene **8** and benzo(*k*)fluoranthene **9**, although the largest HOMO coefficient is indeed located on a type (b) carbon, two  $\Delta H_f^\circ(\text{MH}^+)$  minimum values have been found: one corresponds to the carbon with the largest HOMO coefficient, and no generalization applies to the other. It seems that protonation on a five-membered ring type (b) carbon is less favored.

As expected for acephenanthrylene **7**, the lowest  $\Delta H_f^\circ(\text{MH}^+)$  value is located on a type (a) carbon (Table III). However, two different type (a) carbons—C<sub>8</sub> and C<sub>9</sub>—are available and the lowest  $\Delta H_f^\circ(\text{MH}^+)$  value is found for C<sub>8</sub> with the lowest HOMO coefficient (against rule 2). Steric hindrance cannot be responsible for the protonation site preference as H—H distances are never below 2.5 Å. Examination of the neighboring atomic orbitals gives an explanation for the proton localization. C<sub>8</sub> is preferred because the C<sub>7</sub> HOMO coefficient of 0.324 is much larger than the C<sub>10</sub> (bonded to C<sub>9</sub>) HOMO coefficient of 0.035.

**TABLE IV.**  
Experimental and AM1-Calculated  $\Delta H_f^\circ(\text{MH}^+)$   
(kcal/mol) for Five-Membered Rings PAHs.

Compound	AM1	Exp.	Protonation carbon type
Indene <b>1</b>	209.5	—	a
Acenaphthylene <b>2</b>	239.5	—	a
Acenaphthene <b>3</b>	208.6	199 <sup>a</sup>	c
Fluorene <b>4</b>	224.8	210 <sup>a</sup>	d
Fluoranthene <b>5</b>	255.2	235 <sup>a</sup>	c
Aceanthrylene <b>6</b>	250.4	—	a
Acephenanthrylene <b>7</b>	253.0	—	a
Benzo( <i>b</i> )fluoranthene <b>8</b>	269.5	—	c
Benzo( <i>k</i> )fluoranthene <b>9</b>	269.1	—	c
Benzo( <i>a</i> )fluoranthene <b>10</b>	265.5	—	c
Benzo( <i>j</i> )fluoranthene <b>11</b>	268.3	—	b
Benzo( <i>j</i> )aceanthrylene <b>12</b>	266.6	—	a
Benzo( <i>e</i> )aceanthrylene <b>13</b>	264.2	—	a
Benzo( <i>l</i> )aceanthrylene <b>14</b>	270.3	—	a
Indeno(123 <i>cd</i> )pyrene <b>15</b>	275.2	—	d

<sup>a</sup> From ref. 7.

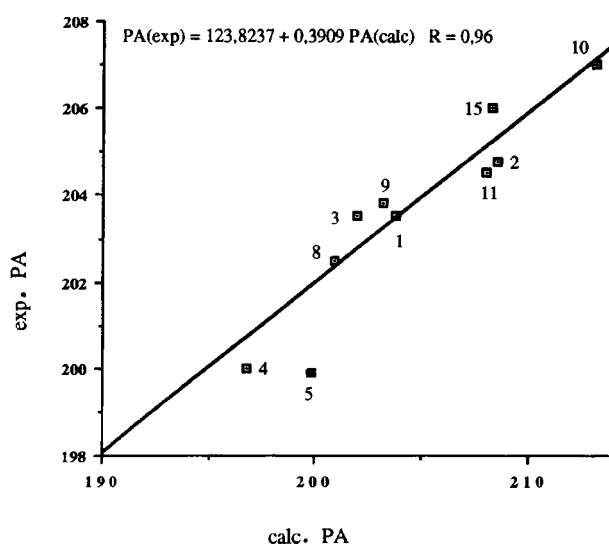
The structure of each molecule with the lowest  $\Delta H_f^\circ(\text{MH}^+)$  value was always selected in our calculations.

### CORRELATION BETWEEN EXPERIMENTAL AND THEORETICAL PAs

PAs of all studied molecules are calculated by relating the computed  $\Delta H_f^\circ(\text{M})$  and  $\Delta H_f^\circ(\text{MH}^+)$  and the experimental  $\Delta H_f^\circ(\text{H}^+)$ , as indicated previously. The  $\Delta H_f^\circ(\text{MH}^+)$  values resulting from AM1 calculations together with the corresponding experimental values given by Lias et al.<sup>7</sup> when available are listed in Table IV. The type of protonation site is also mentioned for each molecule.

A correlation between calculated and experimental PAs is established (Fig. 3). Although only three experimental values were available<sup>7</sup>—acenaphthene **3**, fluorene **4**, and fluoranthene **5**—other experimental data were estimated from ammonia chemical ionization PAHs mass spectra, except for the five commercially unavailable compounds. Our experimental and calculated PAs of PAHs follow a linear relationship. Only fluoranthene **5** PA deviates. We suspect that its published experimental PA<sup>7</sup> was underestimated. We redetermined by diethylether chemical ionization mass spectrometry<sup>15</sup> the fluoranthene **5** PA at 202 kcal/mol. This value fits the regression line.

Table V reports PAs determined by semiempirical calculations after corrections using the correlation equation (Fig. 3) as described in a previous study.<sup>6</sup> The PAs are in good agreement with ex-



**FIGURE 3.** Calculated versus experimental PAs (kcal/mol) of molecules listed in Scheme 1.

**TABLE V.**  
**Calculated and Experimental PAs of Five-Membered-Ring PAHs (kcal / mol).**

Compound	AM1	Exp.	Corrected AM1
Indene <b>1</b>	203.8	203.5 <sup>a</sup>	203.5
Acenaphthylene <b>2</b>	208.5	205 <sup>a</sup>	205.3
Acenaphthene <b>3</b>	201.2	203.5 <sup>b</sup>	203
Fluorene <b>4</b>	196.8	200.0 <sup>b</sup>	200.7
Fluoranthene <b>5</b>	199.9	199.3 <sup>b</sup>	202
Aceanthrylene <b>6</b>	220.0	—	209.8
Acephenanthrylene <b>7</b>	210.1	—	206.0
Benzo( <i>b</i> )fluoranthene <b>8</b>	200.9	202.5 <sup>a</sup>	202.5
Benzo( <i>k</i> )fluoranthene <b>9</b>	203.2	204 <sup>a</sup>	203.5
Benzo( <i>a</i> )fluoranthene <b>10</b>	213.1	207 <sup>a</sup>	207.1
Benzo( <i>j</i> )fluoranthene <b>11</b>	208.0	204.5 <sup>a</sup>	205.1
Benzo( <i>j</i> )aceanthrylene <b>12</b>	219.7	—	209.7
Benzo( <i>e</i> )aceanthrylene <b>13</b>	220.1	—	209.9
Benzo( <i>l</i> )aceanthrylene <b>14</b>	218.1	—	209.1
Indeno(1,2,3 <i>cd</i> )pyrene <b>15</b>	208.3	206 <sup>a</sup>	205.2

<sup>a</sup> Determined in this work.  
<sup>b</sup> From ref. 7.

perimental values for indene **1**, acenaphthene **3**, benzo(*k*)fluoranthene **9**, benzo(*a*)fluoranthene **10**, benzo(*j*)fluoranthene **11**, and indeno(123*cd*)pyrene **15**. Five unknown experimental PAs are established by correcting the AM1-calculated PA using the correlation equation relating experimental and semiempirical PA values:

$$PA_{exp} = 123.82 + 0.39 PA_{calc}$$

**VALIDATION OF AM1 AND AB INITIO CALCULATIONS**

*Ab initio* and semiempirical calculations were performed for indene **1** as previously described. Final geometries optimized by both methods do not differ significantly. Moreover, the site of protonation determined by AM1 after systematic investigation of the different possible protonation sites, is consistent with that given by *ab initio* calculations. The lowest energy was obtained for the same site of protonation in both semiempirical and *ab initio* calculations. Indeed, at the HF/6-31G\* level, the second-most stable structure is 9 kcal/mol higher in energy. This confirms that there is no ambiguity about the protonation occurring on the five-membered ring.

As the HF/6-31G\* level significantly overestimates the PA of indene (216.9 kcal/mol [Table VI], compared to 203.8 kcal/mol with the AM1 calculation) it was necessary to add correlation to the

Hartree–Fock energy. The PA obtained at the MP2/6-31G\*//HF/6-31G\* level was 203.2 kcal/mol (Table VII).

A B3LYP/6-31G\* DFT calculation also was performed. After thermal corrections, the PA at 298 K was 213.8 kcal/mol. This value is about 10 kcal/mol above the MP2/6-31G\*//HF/6-31G\*, the corrected AM1 and the experimental values. An extended basis calculation was attempted at the B3LYP/6-311+G\*\* level. A complexation energy of 214.5 kcal/mol was found (Table VI). The frequency calculation was not tractable with our workstation. However, applying the thermal corrections obtained at the B3LYP/6-31G\* level, the final calculated PA value of indene **1**, 208.2 kcal/mol, is more consistent with the experimental value.

Indene **1** PA (Table VI) are determined at 203.2 kcal/mol, 203.8 kcal/mol, and 203.5 kcal/mol by

**TABLE VI.**  
**PA and Complexation Energy (kcal / mol) Obtained with Different Methods for Indene 1.**

Methods	<i>E</i> <sub>compl</sub>	PA
Experimental	—	203.5
AM1	—	203.8
HF / 6-31G*	–223.8	216.9
MP2 / 6-31G* // HF / 6-31G*	–210.1	203.2
B3LYP / 6-31G*	–220.1	213.8
B3LYP / 6-311 + G**	–214.5	208.2



**TABLE VII.**  
**Ab Initio and DFT Energy Calculations for Indene 1.**

	Indene	Protonated indene	Proton	$\Delta E$
<i>E</i> at 0 K (Hartree)				
HF/6-31G*	−345.462245	−345.818846	0	−0.356601
MP2/6-31G*//HF/6-31G*	−346.608691	−346.943428	0	−0.334737
B3LYP/6-31G*	−347.755711	−348.106547	0	−0.350836
B3LYP/6-311+G**	−347.851063	−348.192869	0	−0.341806
<i>E</i> <sub>therm</sub> (kcal/mol)				
HF/6-31G*	98.42	106.76	0.89	7.45
B3LYP/6-31G*	92.45	100.25	0.89	6.91

AM1, *ab initio* calculations and experimentally with ammonia CI, respectively. The consistency of the three methods is satisfactory.

## Conclusions

AM1 semiempirical calculations allow PA estimates of polyaromatic hydrocarbons with acceptable accuracy. This takes into account the linear relationship between calculated and experimentally measured PAs of the homologous compounds, for correction of AM1-calculated PAs:

$$PA_{\text{correct}} = 0.39 PA_{\text{AM1}} + 123.82$$

Moreover, examination of HOMO coefficients of the different available protonable carbons allows prediction of the preferential protonation sites for all studied PAHs.

Unknown PAs can be obtained at an estimated accuracy of  $\pm 1$  kcal/mol. As discussed elsewhere,<sup>6</sup> AM1-calculated PAs can be used analytically for helping to identify chromatographically unresolved isomer mixtures by chemical ionization mass spectrometry, by measuring the  $[M + 1]^+ / M^{+ \cdot}$  ratio on the mixture mass spectrum.

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